From: Jessica C Beard <jcbeard@mit.edu>
Sent: Monday, October 26, 2020 4:52 PM
To: MORASH, MELANIE
Cc: Bevin P Engelward
Subject: Comment on the proposed Olin cleanup plan
Attachments: MIT SRP response to proposed cleanup plan Aug 2020 20.10.26.docx

Dear Ms. Morash,

My name is Jessica Beard and I'm a chemistry PhD candidate and part of the MIT Superfund Research Program (MIT SRP). I believe you have already received the attached response to the Olin Chemical site cleanup plan from another member of MIT SRP, but there are a couple points in that response I would like to highlight.

First, I am concerned about the efficacy of the "pump-and-treat" strategy for DAPL and LNAPL. Although the individual treatment steps listed for highly contaminated groundwater can be effective, the fact that the treated water is released back into an environment containing material *not yet treated* may allow for re-formation of hazardous chemicals. This may be particularly true of nitrosamines, which often produce their corresponding secondary amines (e.g. dimethylamine from NDMA) during UV treatment; those secondary amines are themselves nitrosamine precursors. The proposed treatment plan says NDMA will be destroyed with "UV photo-oxidation," and I am not clear if this is referring to simply UV irradiation or if the intent is to pair UV light with the addition of an oxidant. If it is the latter case, it has been shown that UV/O_3 can reduce the formation of the secondary amine during photolysis and so re-formation of nitrosamines may be somewhat mitigated.

Second, I would like to emphasize the need to test for additional nitrosamines other than NDMA at this site. Because NDMA itself was not an intentional product at this facility (although other nitrosamines were), it is plausible that other nitrosamines were also formed through the same process or processes which resulted in NDMA. Given that many nitrosamines are probable human carcinogens, regularly monitoring only NDMA may be underestimating the risk to human health.

I appreciate the ability to give this feedback, and hope that it can be helpful moving forward at this site.

Sincerely,
Jessica Beard

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Comment to the EPA regarding the proposed cleanup plan for the Olin Chemical Superfund Site in Wilmington, MA

The Massachusetts Institute of Technology Superfund Research Program (MIT SRP) appreciates the opportunity to provide feedback regarding the EPA's plan for remediating the Olin Chemical Superfund site, proposed in August 2020. Here, we have integrated expertise from our chemists, environmental engineers, and biologists in consideration of the proposed plan.

DAPL interim action

We are pleased that there are proposed interim actions to remediating the dense aqueous phase liquid (DAPL) pool. Given the complexity of the environmental contamination and potential for continued plume expansion and human exposure, interim action is appropriate. We agree that continued quarterly monitoring of the 18 currently tested wells for nitrosamine contamination is appropriate, but should be expanded to include other nitrosamines and contaminants beyond *N*-nitrosodimethylamine (NDMA) only. In addition, we feel it is extremely important to characterize the full chemical composition of DAPL in order to understand the health risks to the community, past, present, and future. We gladly offer to assist in this characterization, and we request a sample of DAPL in order to do so.

One specific concern is the proposed method of "pump-and-treat" for DAPL. Historically, pump-and-treat is ineffective because the entire mass cannot be treated simultaneously, and turnover rates are extremely slow relative to the size and dynamics of the plume. Even if DAPL is treated effectively, upon reinjection it returns to the contaminated plume and facilitates plume migration, and it may still contain precursors that re-form hazardous chemicals. Treated waste must be tested for any potentially hazardous contents before re-release into any environment. As one example, the pump and treat method for remediating trichloroethylene on Cape Cod ultimately has not served to reduce contamination. We encourage the EPA to provide evidence of efficacious pumping and treatment in similar contexts before this method is applied to DAPL.

LNAPL and soil/sediment actions and ongoing nitrosamine formation

The proposed final actions regarding the light non-aqueous phase liquid (LNAPL) and soil/sediment are not satisfactory to our technical experts. As with the DAPL, we are concerned about the efficacy of pumping and treatment for LNAPL. Considering the history of chemical disposal at the site, NDMA precursors and other chemical hazards are likely present in the LNAPL and soil/sediment, and more aggressive assessment and response (e.g., excavation and/or containment) is necessary. Olin manufactured nitrosamine products, namely *N*-nitrosodiphenylamine (aka. Wiltrol N, discussed further below) and a product called "Opex" (dinitrosopentamethylenetetramine), which may be less mobile in the environment than NDMA due to soil sorption, thus necessitating more aggressive soil remediation. The acidity of the site's waste, combined with these manufactured nitrosamines, may create conditions favoring ongoing

formation of more mobile nitrosamines (like NDMA) via trans-nitrosation that could continue to leach into the groundwater.

Additionally, numerous nitrosamine precursors or materials known to create nitrosamine-forming conditions are known or highly likely to be present in the LNAPL and soil/sediment, including: hydrazines (which were manufactured at this site); raw materials for Nitropore 5PT (a product formerly manufactured at this site); aqueous ammonia and chlorine (known contaminants in high levels). Organic hydrazine derivatives are well-established precursors for *N*-nitrosamines, but Olin has been vague about their hydrazine manufacturing conditions and methods for treatment and disposal. Nitropore 5PT (aka Expandex 5 PT, 5-phenyltetrazole) manufacturing utilized sodium nitrite, dimethylformamide (DMF), and strong acid; similar conditions were recently found to be the source of NDMA contamination in the blood pressure medication Valsartan, leading to unacceptable levels of human exposure and prompting recall of the drug. Aqueous ammonia and chlorine, which react to form chloramines, are found at concerningly high levels in both surface and groundwater. Chloramines have long been known to produce nitrosamines from reaction with a wide variety of precursors. All of these chemicals are mobile in the environment and continue to contaminate the site; it is therefore reasonable to expect that these precursors will continue to react and form toxic and carcinogenic *N*-nitrosamines, including NDMA. Over time, this novel formation will reduce the efficacy of efforts to remediate the DAPL and restore the environment of Wilmington. Further, because the slurry wall was not installed to bedrock and leaves opportunity for fluid transport, ongoing NDMA production would continue to contaminate the groundwater of Wilmington until these chemical sources are removed and an effective barrier constructed.

Other nitrosamines (besides NDMA) are important

In addition to our concerns about the proposed remedial actions, we would like to call attention to the importance of monitoring additional nitrosamines in the environment. *N*-nitrosamines, a class comprising hundreds of chemicals, are among the most potent carcinogens known. Over 70 *N*-nitrosamines have been documented to cause cancer in animals, and most of them are not currently tested for at the Olin site. For example, *N*-nitrosodiethylamine (NDEA) is even more toxic and carcinogenic than NDMA, and given its structural similarity, it is almost certainly present at the site, but it does not appear to be routinely measured (Nobis OU3 RI report 2019).

One nitrosamine that contaminates the site and should be a substantial concern is *N*-nitrosodiphenylamine (NDPhA) (not to be confused with *N*-nitrosodi-*n*-propylamine, NDPA. Notably, the abbreviation NDPA is used interchangeably for the propyl and phenyl compounds in many reports). NDPhA was manufactured at the site and has been found in the Olin site LNAPL and groundwater. Although NDPhA does not directly damage DNA (whereas NDPA does), it is an EPA class B2 probable carcinogen, and it is a precursor for NDMA (McGregor 1994, *Mutation Research*). Given the relative thermal instability and low volatility of NDPhA,

GC/MS (or GC/MS/MS) analysis of this chemical is problematic – NDPhA is expected to decompose at the elevated temperatures required for this approach. Thus, results of NDPhA testing at Olin likely underestimate the true level of contamination. Even so, NDPhA has been found at unacceptably high levels (see EPA/Nobis Engineering letter of disapproval March 2018 RI/FS Deliverables). Given the known contamination of the site with additional nitrosamines, and the potential for even more toxic nitrosamines, it is important to take measures in identifying, monitoring, and remediating other nitrosamines in DAPL, LNAPL, and groundwater. The MIT team is developing analytical methods for multiple N-nitrosamines and so it will be important to provide MIT with environmental samples and test well samples.

We appreciate the careful consideration of our concerns by the EPA, MassDEP, and Olin, and we look forward to an improved cleanup proposal following this public comment period. Specific actions that can improve the cleanup plan include:

- Characterization of DAPL contents
    - We will assist in this effort and so receiving a sample of DAPL is critical.
- Critical evaluation of pump-and-treat for DAPL and LNAPL remediation
    - Evidence of efficacy for this method should be established
    - Treated waste must be tested for remaining contaminants and nitrosamine precursors before it is re-released into any environment
- Characterization and remediation of nitrosamine precursors in DAPL, LNAPL, and soil/sediment
- Monitoring ongoing nitrosamine formation and nitrosamine levels over time
    - If nitrosamine concentrations do not decrease significantly on site or in the plume, alternative remediation methods must be identified and applied
- Testing and monitoring of additional nitrosamines beyond NDMA in DAPL, LNAPL, and soil/sediment. The MIT team is developing analytical approaches and will need samples for analysis.
- More aggressive remediation of LNAPL and soil/sediment
    - Build effective barriers, including containment walls that extend to bedrock and permanent, secure, impermeable caps
    - Securely remove and contain contaminated LNAPL and soil/sediment without spreading contaminants beyond the site
- Communicate the intended fate of treated, excavated, or otherwise removed contamination
    - Chemical contaminants should not be transferred to another site that risks human exposure